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Surface Modification of Aluminium Alloy with Super Hydrophobic Characteristics using Immersion and Spray-Coating Method

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Abstract. The surface of a thin aluminum alloy with thickness of 0.103 mm was modified using immersion method to produce high water contact angle of more than 150° which constitutes a super-hydrophobic surface characteristics. Contact angle was measured using a digital goniometer and the modified surfaces were examined under a scanning electron microscope. Apart from immersion technique, spray-coating method was also employed to modify the surface of the aluminum alloy for comparison. The results of surface modification with immersion method shown a higher water contact angle than the spray-coating method by 56%. The weight of the samples were also measured before and after the etching process. Previously, the conventional immersion method is only well-suited for a thick material whereas the thin material can be easily dissolved with the conventional formula. Initial immersion method fully dissolved the thin aluminium alloy strip. Thus, the immersion method was modified and effectively produced a super-hydrophobic surface with contact angle of 160° for the thin aluminium alloy with only 10% weight loss.

1. Introduction

It is widely understood that a surface with water contact angle (CA) beyond 150° is known as super-hydrophobic [1-2]. The super-hydrophobic characteristics are alluring to many researchers due to anti-corrosion, anti-wetting, anti-icing and self-cleaning. Based on the literature reviews [3-12], there are many techniques and methods to produce a super hydrophobic surface.

Controllable immersing method is a simpler and convenient technique to produce the super hydrophobic surface using an etching technique by chemical assistance [3]. Wu's [3] performed the immersion method on an aluminium alloy plate surface with thickness of 1.0 mm. Their samples were cleaned and polished with different grades of sand paper. Next, the samples were investigated in different composition of chemicals: hydrochloric acid (HCl), oxalic acid ($C_2H_2O_4$) and acetic acid (CH_3COOH). They also used potassium permanganate ($KMnO_4$) and stearic acid ($C_{18}H_{36}O_2$) to further stabilize and reduce the surface energy, respectively [3]. They achieved a maximum CA of 166°±1.8°. Alternatively, the super hydrophobic can be produced by spray-coating or anodizing a layer of thin film polymer on the surface where the polymer has the

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capability of self-assembling into a certain hierarchical pattern. This spray-coating method is detailed in other research papers [11-13]. Nevertheless, the main drawback of the spray-coating method is the film would be easily peeled off due several factors such as interfacial friction, and ultra-violet (UV) degradation.

In present study, the controllable immersing method [3] was used to modify the surface properties of a thin aluminium alloy with thickness of 0.103 mm. This, by far, has a relative thickness of 10 ten times less than the material used in literatures [3,7,9]. Understandably that the chemical etching method would dissolve some of the surface material to form hierarchical patterns on the material surface. In most of the literatures [3-11], it was not reported on the amount of material losses due to the chemical etching process as this is crucial when a thin material is used for etching process. Thereby, it is critical to determine a proper immersion technique to produce a high water contact angle on a thin aluminium without too much material losses due to etching process on a thin material, i.e. thickness of 0.103 mm.

This paper first explains on comparison between the immersion and spray-coating method. Secondly, a discussion on the immersion method employed on two different surfaces, aluminium alloy and copper alloy. Two compositions of etching solution with 5% and 7.4% HCl of a modified immersion method for thin aluminium alloy strip were discussed at different immersion time, which varied from 0.5 hrs to 18 hrs subsequently.

2. Method of Preparation

A detailed preparation for immersion method is reported in Wu et al. [3], and as a summary of the process, the immersion method comprises of four stages: cleaning, etching, stabilizing, and modifying. Throughout the experiments, all samples underwent cleaning stage on both sides of the surface with industrial abrasion paper of different grades from #220, #600, #800 and #1200, respectively in the sequence from low to high grade. The chemical used for the etching process: 2 mol/L hydrochloride acid (HCl),
0.16 mol/L oxalic acid, 1.61 g stearic acid with 2% ethanol, and 0.2 mol/L potassium permanganate ($KMnO_4$). The volume ratio for HCl and oxalic acid is 1:1. Potassium permanganate ($KMnO_4$) was used to stabilize the surface. Stearic acid is used to further reduce the surface energy as surface modification.

As aforementioned, the preliminary study was focused on comparing the surface water contact angle using two immersion and spray-coating method, respectively. The substrates for spray-coating method were obtained commercially from MetalGard (Malaysia) and it is a spray-on method valid for metal surfaces only. The manufacturer claimed a high contact angle of more than 100°. The samples used were aluminium alloy with thickness of 3.0 mm. Two samples were prepared. The first sample was prepared with immersion method whereas the second sample were sprayed arbitrarily with distribution based on visual inspection. The commercial substrates were applied to the surface with an air-compressor gun spray. The substrates were left to dry for a day, and coating was re-applied to ensure a uniform distribution on the surface. A total of two layers of coating were applied on the second sample.

Secondly, two metal alloy, aluminium and copper, with thickness of 3.0 mm and 0.9 mm, respectively was compared using immersion method. The dimension of both alloys is 40 × 40 mm. The same immersion method was employed to both materials as detailed in the first part of the study. Next, the immersion method was varied in composition and time of immersion to determine an optimum immersion formula for a thin aluminium alloy 2100 with thickness of 0.103 mm for a size of 40 × 40 mm. The thin aluminium alloy samples were provided by Daikin R&D Malaysia Sdn Bhd. On this section, the time of immersion were varied from 18 to 0.5 hours, and then, the concentration of the chemicals were varied based on an optimum time as shown in Table 1 below. In all of the immersion method, the apparatus consisted of a retort stand, a beaker and an additional clamp for sample holding.

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Table 1. Immersion formula variation as a function of time and composition.

Immersion iteration, #	Time, (hours)	Composition	Remarks
	18.0	7.4% HCl and oxalic acid	
1	1.50	$KMnO_4$ (0.20 mol/L)	
	2.00	Stearic acid (0.16 mol/L)	
	6.00	7.4% HCl and oxalic acid	
2	1.50	$KMnO_4$ (0.2 mol/L)	
	2.00	Stearic acid (0.16 mol/L)	Change in the time of immersion for etching process.
	1.00	7.4% HCl and oxalic acid	
3	1.50	$KMnO_4$ (0.2 mol/L)	
	2.00	Stearic acid (0.16 mol/L)	
	0.50	7.4% HCl and oxalic acid	
4	1.50	$KMnO_4$ (0.2 mol/L)	
	2.00	Stearic acid (0.16 mol/L)	
	1.00	5% HCl and oxalic acid	
5	**1.50**	$KMnO_4$ (0.2 mol/L)	
	2.00	Stearic acid (0.16 mol/L)	
	1.00	5% HCl and oxalic acid	Change in molarity of HCl, and time of immersion for $KMnO_4$ and stearic acid.
6	**3.00**	$KMnO_4$ (0.2 mol/L)	
	2.00	Stearic acid (0.16 mol/L)	
	1.00	5% HCl and oxalic acid	
7	**3.00**	$KMnO_4$ (0.2 mol/L)	
	1.00	Stearic acid (0.16 mol/L)	

2.1. Contact Angle Measurement

The contact angle of a water droplet on the modified metal alloy was measured using an optical tensiometer (Theta Light, Attension) with maximum resolution of 1984 × 1264 pixels. During the measurements, the device was set to provide sessile droplet of 3 μL on the sample surface. On each sample, six measurement locations were selected arbitrarily as shown in Figure 1. A sessile droplet of water was syringed onto the surface and the images were recorded at 12 fps and the sequence was repeated in triplicate on all six prescribed locations. Contact angles measurement on both the left and right sides of sample were performed, respectively (see Figure 1).

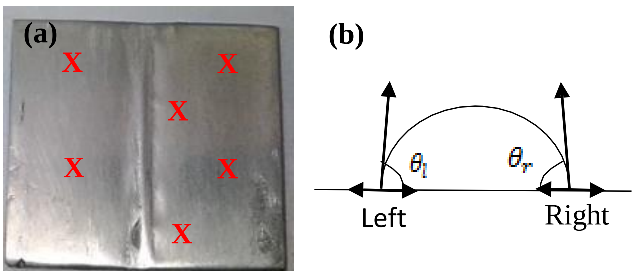

Figure 1. (a) Location selected arbitrarily around marked areas for contact angle measurements, and (b) contact angle of left side, θ_l and right side, θ_r , respectively.

2.2. Surface Wettability Model

The surface wettability of substrates can be evaluated by using several well-known models by *Young*'s equation, *Wenzel*'s equation, and *Cassie*'s equation as outlined in various papers [2]. In the present analysis, the data obtained is fitted with *Young*'s equation as shown:

$$\cos\theta = (\gamma_{SV} - \gamma_{SL}) / \gamma_{LV} \tag{1}$$

2.3. Scanning Electron Microscope (SEM)

The surface-modified thin aluminium alloy sample with super-hydrophobic properties was viewed in a field emission scanning electron microscope (SEM) (Zeiss Ultraplus FE, UK). The microscopic image was recorded at 500× and 1000× magnification at a resolution of 1024×768 pixels. The emission rate of the device is rated at 20 kV. The surface of a thin aluminium alloy with super hydrophobic characteristics for sample #7 is shown in Figure 2(a) and (b) with magnifications of 500× and 1000×, respectively. Figure 2(c), (d) and (e) are the comparison against surface patterns from literatures [3,7,14] which shown to have similar hierarchical patterns, and in this study, the modified surface of a thin aluminium shown to have flower-like patterns.

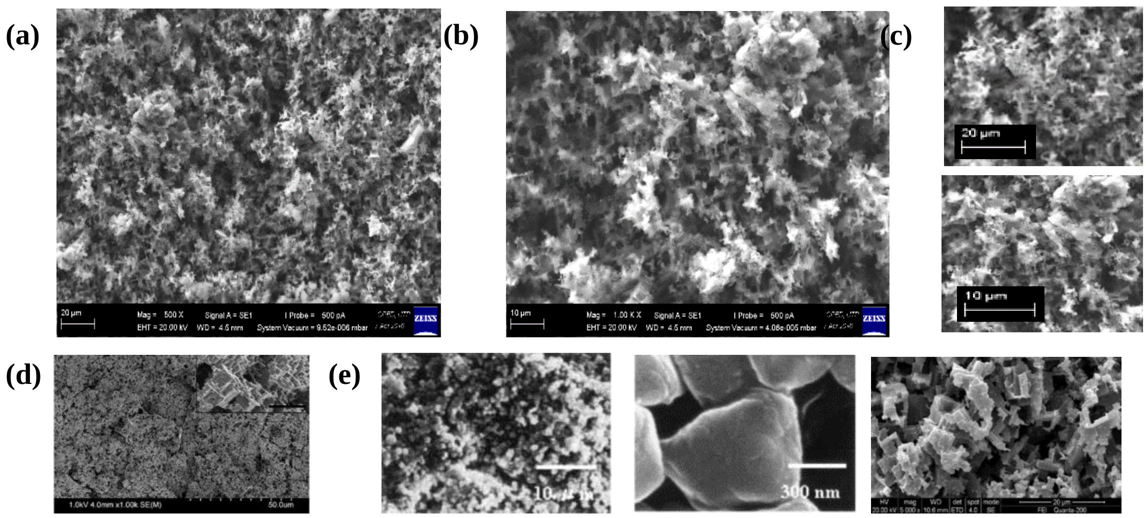

Figure 2. SEM results at (a) 500× and (b) 1000×, and compared to various literature: (c) this study, (d) A. Esmaeilirad et al. [7], (e) T. Kako et al. [14], [f] R. Wu et al. [3].

2.4. Mass Loss Measurement for a Thin Aluminium Alloy

The mass of the thin aluminium alloy samples based on Table 1 was measured before and after the etching process using a precision weighing scale (GF-600, A&D) with measurement uncertainty of ± 0.001 g. As shown in Figure 3, the average mass before and after etching process were weighted at 0.406 ± 0.01g, and 0.353 ± 0.01g, respectively. The mass loss was the highest at 6 hours of immersion with 24% reduction as shown in sample #3. At a lower immersion time of 0.5 hours (sample #5), the mass loss of the aluminium alloy was at 10%. On the other hand, a lower concentration was further reduced from 7% to 5% (sample #7), the mass loss only by 6%. Although, a shorter period of immersion and lower concentration are preferable to avoid mass loss, the water contact angle of the surface will be greatly affected which is elaborated in next section.

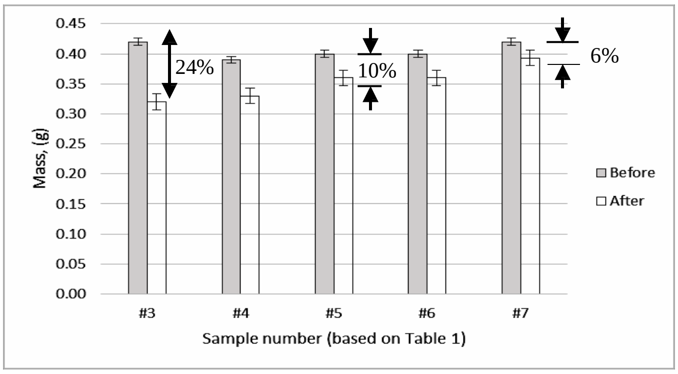

Figure 3. Mass measurement of a thin aluminium alloy specimen before and after the etching process.

3. Results and Discussion

The physical appearance for the control sample and surface-modified aluminium and copper samples are shown in Figure 4. The control sample was used as baseline. The aluminium surface with spray-coating method appears glossy and shiny. In contrast, the aluminium surface with immersion method appears dull and rough. The dullness is expected due to etching process by the acids, and the glossy surface is due to the additional layer of polymer substrate.

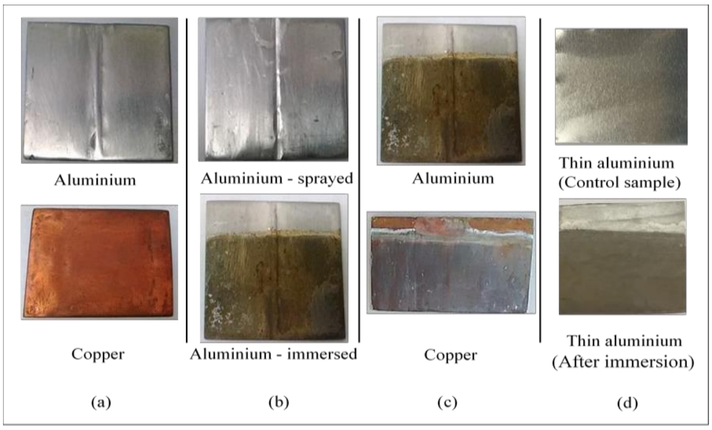

Figure 4. (a) Control samples, (b) aluminium with spray-coating and immersion method, (c) immersion method for aluminium and copper alloy, and (d) immersion method for thin aluminium alloy.

3.1. Comparison between Immersing and Coating Method

The water contact angles on the aluminium alloy using immersion and spray-coating method were 158.2°±2°, and 101.2°±2°, respectively. The contact angle of a control sample of aluminium alloy, was measured at 102.6°. The commercial substrate is only able to modify the contact angle insignificantly around the base line, and this is expected based on the reported contact angle by the manufacturer, which is larger than 100°. However, the water contact angle on the surface-modified aluminium alloy sample was increased by 54% using immersion method as compare to the base sample. It had achieved the desirable contact angle with a super-hydrophobic characteristic, as shown in Figure 5.

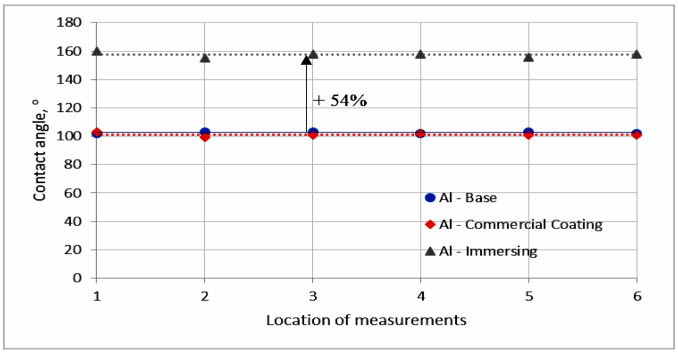

Figure 5. Water contact angle measurement for different techniques.

3.2. Comparison between Aluminium and Copper Alloy using Immersion Method

The water contact angle for aluminium and copper alloy, whose surfaces were modified with immersion method, is shown in Figure 6. Results revealed that the immersion method shows promising super-hydrophobic characteristic for both materials, aluminium alloy and copper alloy with contact angle of 157.0°±2° and 159.0°±2°, respectively. Thus, the immersion method performs well for a copper alloy surface as compared to an aluminium alloy surface based on contact angle.

3.3. Iterations of Immersion Method for a Thin Aluminium Alloy

As shown in Figure 6, the contact angle of 157° was preliminary obtained using immersion method, the initial concentration and immersion time were tested on a thin aluminium alloy sample with a thickness of 0.103 mm which were fully dissolved in the solution due to etching process. In the next iteration, the process was varied by changing the time of immersion and formulation (see Table 1). As a result, only iteration #3, #4, #5, #6 and #7 responded positively without fully dissolving the thin aluminum strip.

By using initial formula, the immersion time using 7.4% HCl and oxalic acid was varied from 0.5 to 18 hours as illustrated in Figure 7. The effect of etching time became significant at 30 minutes and the contact angle is further increased to 161° after 1 hour of immersion. However, the thin alumnimium sample was fully dissolved after 6 hours of immersion.

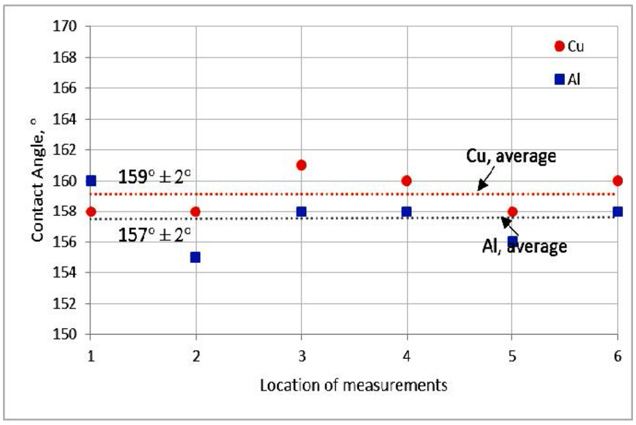

Figure 6. Water contact angle for aluminium alloy and copper alloy.

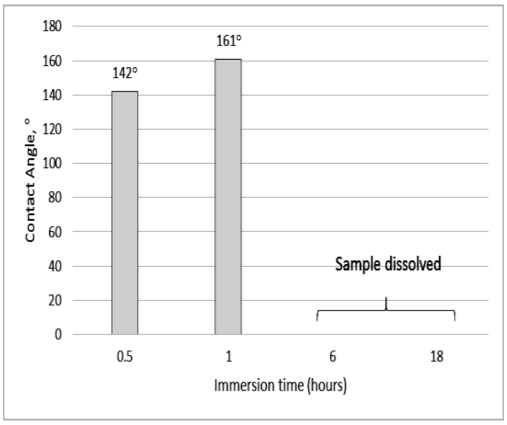

Figure 7. Immersion time for 7.4% HCl.

Next, the concentration of HCl was further varied at 7.4% and 5.0% for 1 hour of sample immersion, respectively. The result shown in Figure 8 indicates that a lower concentration, 5.0% HCl produces a lower contact angle of 150° as compare to a 7.4% HCl with contact angle of 161°. Though, the immersion at the stage of etching is confirmed at 1 hour, the subsequent stage of immersion for surface stabilizer ($KMnO_4$) and surface energy reduction (stearic acid) can affect the final surface morphology. The results of contact angle due to the immersion time for $KMnO_4$ and stearic acid are illustrated in Figure 9.

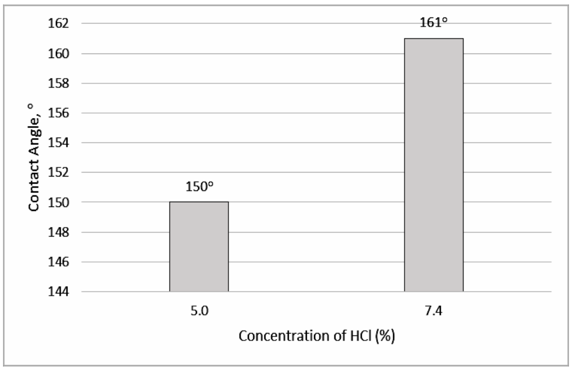

Figure 8. Different concentration of HCl at 7.4% and 5.0%.

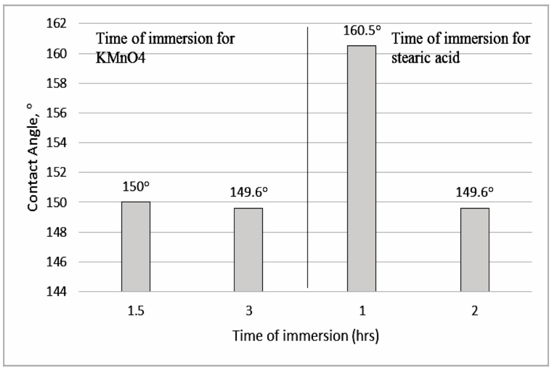

Figure 9. Different times of immersion for $KMnO_4$ and stearic acid.

As seen in Figure 9, the initial time of immersion for $KMnO_4$ is at 1.5 hours. Upon increasing the immersion time from 1.5 to 3 hours, the result yields slightly lower contact angle by 0.2% at 149.6°. When the immersion time of stearic acid is reduced from 2 hours to 1 hour, the contact angle increases from 149.6° to 160.5°. Therefore, varying time of immersion using $KMnO_4$ does not affect much on the contact angle but immersion time using stearic acid greatly reduces the surface energy as much as 7.3% which is shown by the increase of contact angle.

4. Conclusions

Based on several iterations on the substrate concentration and time of immersion, a thin aluminium strip 2100 with thickness of 0.103 mm is produced with super hydrophobic characteristics. Several conclusions are that:

i. A minimum mass loss of 10% is attained due to etching process to produce a high water contact angle.
ii. A thin aluminium with super hydrophobic is achieved with iteration #3 which shows a high contact angle of 160.5°.
iii. SEM results show flower-like patterns due to this modified immersing method.

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